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Mechanism of Stress-Corrosion Cracking in Face-Centered-Cubic Metal

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Introduction

The purpose of the research was to attempt an evaluation of those structural parameters which are possibly significant in giving rise to the phenomenon of stress-corrosion cracking in face-centered-cubic metals. Stress-corrosion is not confined to face-centered-cubic metals, but it is a common mode of failure in various structurally important alloys of this type, eg. copper-base solid solutions such as alpha brass and aluminum bronze,and austenitic stainless steels. Also, the deformation characteristics of face-centered-cubic crystals are relatively well understood compared with those of other structures. Parameters to be investigated included dislocation configurations, stacking faults and energies, and long and short-range order.

The first significant contribution to structural aspects of stress-corrosion was by Forty[1], who attempted to apply theories of imperfections to the twin phenomena of crack nucleation and crack growth, briefly as follows. Crack nucleation in an alloy such as alpha brass was postulated to occur at embrittled sites, perhaps due to dezincification. At these locations a high concentration of vacant lattice sites was assumed to cause embrittlement and permit crack formation. Subsequent crack propagation theory was based on a "restricted slip" model, i.e. a model in which dislocation mobility was impaired by specific properties of the matrix. Forty suggested that the presence of short-range order should reduce dislocation mobility to the point where the high stress concentration at the crack tip could not be relieved --- by dislocation movements --- sufficiently rapidly to prevent brittle crack propagation.

Modifications of this restricted slip theory have been advanced. For example, Robertson and Tetelman[2] discuss the importance of low stacking fault energy in promoting stress-corrosion susceptibility. A low stacking fault energy implies difficulty in cross-slipping, with resultant dislocation pile-ups at grain boundaries and twin boundaries. Such pile-ups have been observed in several stress-corrosion-susceptible alloys, including stainless steels[3] and copper-base solutions[4]. If dislocation pile-ups are significant, it is not known whether cracking proceeds mechanically, for example by the Stroh mechanism[5], or whether unusually rapid electrochemical dissolution occurs along the active slip planes.

The above theories formed the background for the research described in this report.

Stress-corrosion of Copper-Gold Single Crystals

There were several reasons for choosing the copper-gold system for study. Firstly certain compositions can be prepared in states of long-range and short-range order, c.f. Forty's theory, and, secondly, earlier studies by Graf[6] using polycrystals showed a complicated effect of composition; the stress-corrosion susceptibility increased as the gold content increased up to about 25 at %, and thereafter decreased again with increasing gold content. Thus, Graf obtained a U-shaped lifetime curve with a minimum lifetime at 25 at % gold. This behavior did not fit the various stress-corrosion models, and has been assumed by the present writer to involve a complicating effect of grain boundaries.

The copper-gold single crystals used in the present research showed a different, and simpler, compositional dependency. The lifetime of quenched, i.e. short-range ordered, crystals decreased with increasing gold content until at about 30 at % gold the alloys abruptly became immune to attack; this latter composition coincides with Tammann's "parting limit" at which general corrosive attack ceases. The effect of order/disorder phenomena was investigated for the alloy $AuCu_3$. Long-range and short-range ordered crystals, and crystals treated to produce ordered domains of different size, displayed essentially similar stress corrosion lifetimes.

In terms of current theories these results are somewhat difficult to explain in terms of one specific model. Firstly, the stacking fault energies of disordered and ordered $AuCu_3$ are not low[7,8], and so planar dislocation distributions incorporating pile-ups cannot be expected on this account. Nevertheless, this type of dislocation distribution is observed in short-range ordered $AuCu_3$[8], and a reason for its presence must be sought.

it can be explained as follows. Initial slip in a short-range ordered lattice requires a high stress to destroy the local order; this means that subsequent dislocations will move more easily through these disordered regions since they can move under a lower stress. Thus a yield point is observed in these crystals, the upper yield stress being the stress to initiate dislocation movement, and the lower yield stress being the stress to move additional dislocations on the same slip planes. The reason for stress-corrosion susceptibility in long-range ordered $AuCu_3$ is less obvious since the dislocation configuration is not planar. A disturbing feature of these observations is that, as already noted, long-range and short-range ordered Cu_3Au crystals have about the same stress-corrosion susceptibility. This is difficult to account for on a dislocation model since the dislocation distributions are quite different in the two cases.

The above-described work on copper-gold crystals has been submitted for <u>publication in the Journal of the Institute of Metals</u>, but the publication date is not known at this time.

<u>Stress-corrosion of Silver-Gold Single Crystals</u>.

In the case of this system also, Graf[6] obtained a U-shaped stress-corrosion lifetime curve with a minimum lifetime at about 25 at % gold. Since Graf's work was again done with polycrystals it was thought that grain boundaries probably caused a complicated compositional dependency, and that the system should be re-examined using single crystals. Results very similar to those given by copper-gold crystals were obtained, i.e. a decreasing lifetime with increasing gold content, and a minimum lifetime (at about 20 at % silver) which corresponded with the abrupt cessation of susceptibility. However, the lifetimes of susceptible silver-gold crystals are considerably greater than those of susceptible copper-gold crystals (hours instead of minutes) and this can be tentatively explained as follows. Thin-film transmission electron microscopy of silver-gold alloys has been carried out using the HITACHI HU II recently installed in the Department of Minerals and Metals Engineering, University of Wisconsin. Planar dislocation configurations have been found only in the alloys containing 15 and 20 at % gold, and even in these alloys the planar configuration does not dominate the dislocation structure. Most dislocations form tangles or exist as isolated dislocations. In the remaining alloys no pile-ups at all are evident. These observations seem to account for the stress-corrosion behavior of the silver-gold alloys, and perhaps explain why these alloys are less susceptible to stress-corrosion than the corresponding copper-gold compositions. Namely, short-range ordered Cu_3Au (and presumably other copper-gold alloys) has a markedly planar dislocation grouping[8] as required by the restricted slip model.

Silver-gold alloys do not contain appreciable short-range order, and so the observed pile-ups in Ag/15^a/oAu may be due to a lowering of the stacking fault energy. Since isolated dislocations are clearly split into partials, this latter explanation is probably correct.

The work on stress-corrosion properties of silver-gold alloys will shortly be presented for publication.

Research in Progress

Since the research supported by AF-AFOSR-61-68 is being continued with the support of AF-AFOSR-221-63 it is appropriate to review work in progress, and research plans.

A potentiostat has been constructed for making observations on surface films and their effect on stress-corrosion. Forty has recently [9] commented on the importance of tarnish films in the stress-corrosion of alpha-brass, and it cannot yet be considered proved that stress-corrosion is principally a dislocation phenomenon. There is considerable electrochemical evidence that stress-corrosion is associated with oxide films which break down locally permitting corrosive attack, and it may be that surface films and planar dislocation structures are both necessary to stress-corrosion.

Thus work is now in progress on silver-platinum and silver-cadmium single crystals, copper-base (copper-zinc, copper-aluminum, copper-germanium and copper-gallium) polycrystals, and high-purity stainless steels, which seeks to obtain an understanding of the relative importance of structural (dislocation structures) and electrochemical (surface films) effects in causing stress-corrosion.

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